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PROSPECTS FOR EXPANDING THE RAW MATERIALS RESOURCES FOR CERAMIC PRODUCTION

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A technology for producing decorative construction ceramics — red tiles with different tones based on red-burning clay — has been developed. Complex additives consisting of production wastes (aluminum-co-balt-molybdenum catalysts) and wollastonite, which contain color-carrying, strengthening, and sinter-improving oxides, were used. This makes it possible not only to activate the sintering process but also obtain construction ceramic in a wide range of colors as well as to solve the problem of recycling production wastes and expanding the raw materials resources for manufacturing ceramic articles.

Key words: clay raw material, red-burning clay, recycling production wastes, construction ceramic.

It is impossible to imagine modern production of building materials and articles without new and effective solutions to scientific and technological problems in this field. For this reason, construction ceramics must meet ecological, resource-conserving, economic, and design requirements.

A characteristic feature of the modern raw materials base for ceramics is that the total stocks of high-quality clays and kaolins are exhausted. As a result, low-grade local clay rock must be used in production and the adequacy of the supplies determines their importance for developing the production of ceramics with colored sherds.

Questions concerning the expansion of applications for unconditioned plastic raw materials as well as nonplastic natural silicate raw materials and technogenic wastes in the production of construction ceramic materials become especially topical [1-3].

Systematization of the accumulated experimental material on the study and use of clay rocks from Uzbekistan shows that they are represented by almost all forms of clay raw materials: kaolins, white-burning plastic and refractory kaolin clays, light-burning refractory and red-burning low-melting clays and loamy clays with different technological properties and all forms of ceramic material that are promising for manufacturing.

Practically all samples of light-burning clay materials are plastic clays with clayey particle content ($< 5 \mu m$) from 50 to

85%.³ The red-burning clayey raw material possesses more diverse grain composition and comprises dusty clays with clayey material content from 30 to 45% as well as dusty loamy clays in which the clayey fraction varies from 10 to 20%. All clayey material analyzed are polymineral compositions with kaolinite predominating in a mixture with clayey minerals in light-burning clays, while for red-burning clays it is characteristic for montmorillonite to predominate over hydromica and kaolinite. This is the main reason for their high sensitivity to drying and makes it necessary to increase the crack-resistance of green articles based on them by adjusting the effective additives.

The experimental data accumulated from the study of low-melting red-burning clayey raw materials attests that practically all of these rocks are low-melting clays and cover loams with variegated material composition.

To choose clayey initial material for specific ceramic technologies it is necessary to know the interrelation of the composition, properties, and applications of the clays initial materials. This makes it possible to determine ways to regulate its main technological properties.

Specifically, the suitability of clayey initial materials for fabrication of ceramics with colored sherds (construction ceramic) is determined from the following:

the granulometric composition — these are dusty clays (clay fraction content 30 - 45%) and dusty loams (clay particle content 10 - 30%);

the mineral composition — these are low-melting clayey raw materials with complex material composition; the

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³ Here and below — the content by weight.

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TABLE 1.

Material -	Content, wt.%														
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K ₂ O	${\rm TiO_2}$	CoO	MnO	P_2O_5	MoO_3	WO_3	SO_3	other
Parkentskoe clay	49.29	16.47	7.16	14.45	3.66	1.25	1.95	0.67	_	_	_	_	_	0.06	5.04
Wollastonite	53.30	2.27	1.30	38.60	1.40	0.10	0.53	0.10	_	_	_	_	-	_	2.40
Wastes from cata-		65.00	1.05	0.56	0.10	6.00	0.06	0.04	2 02	0.02	0.20	2.10	0.04	1.50	10.44
lyst production	8.45	65.00	1.37	0.56	0.10	6.83	0.06	0.04	2.03	0.02	0.38	2.10	0.84	1.78	10.44

TABLE 2.

	Content, wt.%, in composition					
Component –	1	2	3			
Red clay	70	77	90			
Wastes from catalyst production	17	16	7			
Wollastonite	13	7	3			

coarse-grained part is a mixture of quartz, feldspars, ferruginous minerals (usually in the form of iron oxide and its hydrates, less often in the form of iron carbonate and sulfides) predominately of the montmorillonite type;

the chemical composition — these are acidic and semiacidic clayey raw materials with composition in the calcined state (%): $10-20 \text{ Al}_2\text{O}_3$, $65-76 \text{ SiO}_2$, 10-20 fluxes, including $> 3\% \text{ Fe}_2\text{O}_3$.

By the nature of their effect in ceramic mixes non-plastic silicate additives of natural and technogenic origin can be conventionally divided into brightening, strengthening – reinforcing (calcium-magnesium-silicate raw materials — wollastonite and dolomite rock), and color-carrying additives — industrial wastes.

Wollastonite is a natural calcium silicate with chemical formula $CaSiO_3$ possessing valuable and sometimes unique properties. Specifically, needle – fiber habitus of the wollastonite crystals with long $20-200~\mu m$ needles, which remains when heated to temperatures $1000-1100^{\circ}C$, determines the possibility of using wollastonite rocks as a structure-forming additive that has a reinforcing – strengthening effect for obtaining stronger ceramic materials.

Another feature of wollastonite is that volume of articles made from it does not change during the manufacturing processes.

The present article presents the results of research on the development of a technology for producing decorative construction ceramic articles. Composite, colored, ceramic files and bricks have been obtained using local clayey raw materials (red-burning clay from the Parkentskoe deposit), local raw materials, and technogenic wastes. The chemical composition of the raw materials employed is presented in Table 1 and the mix composition for red floor tiles is presented in Table 2.

To obtain red construction ceramic with different color tones wastes from the production of aluminum-cobalt-molybdenum catalysts from "MOVOMET" JSC were introduced as a color-carrying component, and VK-1 wollastonite

TABLE 3.

T. I.	Additive-free	Amount of wastes from catalyst production, %					
Indicator	clay	7	16	17			
Water absorption, %	21.6 – 22.8	2.58 - 2.66	2.36 - 2.39	1.80 - 1.40			
Coefficient of sensitivity to drying	2.20	0.11 - 0.22	0.09	0.09			
Air shrinkage, %	8.22 - 8.66	4.50 - 4.9	2.90 - 3.30	2.50 - 2.90			
Shrinkage of sintered sample, %	16.90 - 17.00	9.90 - 10.90	8.92 - 8.95	7.60 - 7.90			
Bending strength, MPa:							
dry materials	0.89 - 0.92	1.17 - 1.34	1.36 - 1.54	1.50 - 1.64			
calcined materials	10.21	14.94	16.35	16.39			
Calcination temperature, °C	1050 - 1100	1050 - 1100	1050 - 1100	1050 - 1100			
Ceramic color after calcination at temperature, °C:							
1050	Reddish	Red-brown	Red-brown	Claret			
1080	Red	Dark red brown	Claret-brown	"			
1100	Dark red	Brown	Red	Claret-brown			

concentrate (Koitashskoe wollastonite) was introduced as a strengthening component.

Our studies made it possible to develop a technology for obtaining red construction ceramic with different color tones from red-burning clayey rocks. A combination of the following operations results in the activation of structure-forming processes and formation of the color of ceramic mix based on low-melting red-burning raw materials combined with the introduction of a strengthening additive — wollastonite concentrate. A complex mineral additive consisting of wollastonite and wastes from the production of aluminum-cobaltmolybdenum catalysts with a clay additive is prepared by the slip method in a ball mill to residue no more than 2-5% on a No. 006 sieve. Next, the slip is mixed with the main clay. The ceramic mix is carefully homogenized and allowed to age, which is necessary to ensure that the mass-transfer processes and, in consequence, the reactions resulting in the synthesis of the red iron-containing compounds go to completion. After spray drying to moisture content 5-6% the slip is subjected to semidry pressing in two stages: 3-5 and 30 - 35 MPa.

The effect of the wastes from the production of aluminum-cobalt-molybdenum catalysts on the properties of ceramic articles from red-burning clays is reflected in Table 3. Evidently, the use of a complex additive, consisting of wastes from the production of aluminum-cobalt-molybde-num catalysts and wollastonite, containing color-carrying, strengthening, and sinter-improving oxides, in ceramic mix based on red-burning clay from the Parkentskoe deposit makes it possible not only to activate sintering but also to obtain construction ceramic in a wide range of colors as well as to solve the problem of recycling production wastes and expanding the raw materials resources for manufacturing ceramic articles.

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